

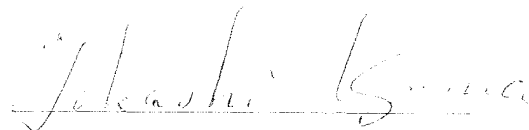


C E R T I F I C A T I O N

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Dated this 28th day of May, 2003


Takashi KOJIMA



(Translation)

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Application Number: Japanese Patent Application
No. 2001-042717

Applicant(s): Shin-Etsu Chemical Co., Ltd.

August 24, 2001

Commissioner,
Patent Office

Kozo OIKAWA
(sealed)

Certificate No. 2001-3076014

2001-042717

[Paper]	APPLICATION FOR PATENT
[Reference Number]	12665
[Application Date]	February 20, 2001
[Destination]	The Commissioner of the Patent Office Kozo OIKAWA
[International Patent Classification]	C08L 83/05
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[List of Documents Attached]

[Document] Specification 1

[Document] Drawing 1

[Document] Abstract 1

[Necessity of Proof] Yes

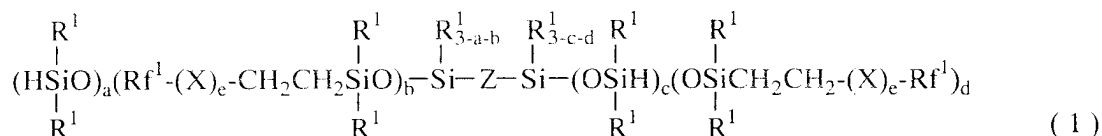
2001-042717

[SPECIFICATION]

[TITLE OF THE INVENTION] Fluorinated Organosilicon Compounds

[CLAIMS]

- 5 [Claim 1] A fluorinated organosilicon compound having the following general formula (1):



wherein R^1 is independently a monovalent hydrocarbon group having 1 to 6 carbon atoms,

- 10 X is independently $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{OCH}_2-$ or $-\text{Y}-\text{NR}^2-\text{CO}-$ wherein Y is $-\text{CH}_2-$ or a divalent group of the following structural formula (I), and R^2 is hydrogen or a monovalent hydrocarbon group having 1 to 10 carbon atoms,

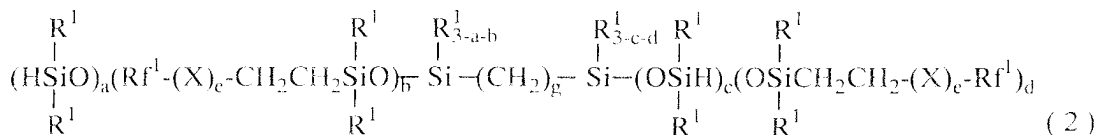
- 15 Rf^1 is a monovalent perfluoroalkyl or perfluorooxyalkyl group,

Z is a divalent hydrocarbon group of 1 to 15 carbon atoms which may contain an ether bond,

- subscripts a, b, c and d are integers satisfying
 $a \leq 3$, $b \leq 3$, $c \leq 3$, $d \leq 3$, $3 \leq a+c \leq 5$, $1 \leq b+d \leq 3$, $a+b \leq 3$,
 20 and $c+d \leq 3$, and e is independently 0 or 1:



[Claim 2] The fluorinated organosilicon compound of claim 1 having the following general formula (2):



wherein R^1 , X, Rf^1 , a, b, c, d and e are as defined above and g is an integer of 1 to 8.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

This invention relates to novel fluorinated
5 organosilicon compounds useful as a crosslinking agent for
addition reaction.

[0002]

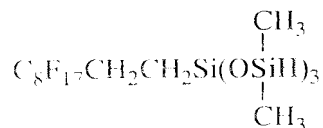
[Prior Art and Problem to be Solved by the Invention]

Rubber compositions of the addition reaction curing
10 type generally contain a base polymer having alkenyl groups
such as vinyl groups, a compound having hydrogen atoms
directly attached to silicon atoms (i.e., SiH groups), and
an addition reaction catalyst such as a platinum group
catalyst. Cure takes place through the addition of the SiH
15 groups to the alkenyl groups on the base polymer.

[0003]

Organosilicon compounds having SiH groups are known in
the art. For example, JP-A 3-197484 discloses an
organosilicon compound of the structure that a SiH group is
20 attached to a silicon atom having a fluoroalkyl substituent
through an oxygen atom, as shown by the following formula.

[0004]



[0005]

This compound is capable of hydrosilylation reaction
25 with vinyl group-bearing compounds, and it is a useful raw
material from which various derivatives are synthesized.
For example, modifiers, crosslinking agents for resins and
rubber, surfactants, and additives can be synthesized from
this compound.

30 [0006]

However, the use of this compound as a crosslinking
agent gives rise to the problem that the compound is likely

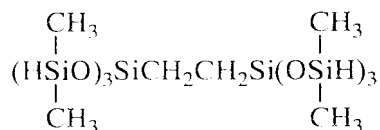
to volatilize upon curing at elevated temperatures so that cured properties become unstable.

[0007]

A compound of the following formula is also known.

5 When this compound is used as a crosslinking agent in a composition comprising as a base polymer a polymer having a high fluorine content such as perfluoropolyether, the composition lacks storage stability and cure stability because of poor compatibility between the components.

10 [0008]



[0009]

The present invention has been done in view of the above circumstances. An object of the invention is to provide a novel fluorinated organosilicon compound having
15 SiH groups capable of hydrosilylation reaction with such compounds as vinyl group-bearing fluoro-polymers in a stable manner and fully compatible therewith.

[0010]

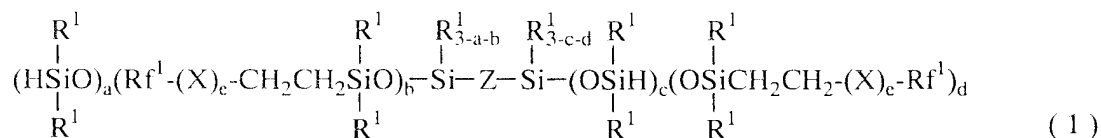
[Means for Solving the Problem and Embodiment of the
20 Invention]

The present inventors have earnestly studied in order to attain the above object. As a result, it has been found that a fluorinated organosilicon compound having at least one fluorinated organic group and at least three SiH groups
25 in a molecule as shown by the general formula (1) below is capable of hydrosilylation reaction with such compounds as vinyl group-bearing fluoro-polymers in a stable manner and is fully compatible with such polymers. The present invention has been completed by the above finding.

30 [0011]

Accordingly, the invention provides a fluorinated organosilicon compound having the following general formula (1).

[0012]



Herein R^1 is independently a monovalent hydrocarbon group having 1 to 6 carbon atoms; X is independently $-CH_2-$, $-CH_2O-$, $-CH_2OCH_2-$ or $-Y-NR^2-CO-$ wherein Y is $-CH_2-$ or a divalent group of the following structural formula (I), and R^2 is hydrogen or a monovalent hydrocarbon group having 1 to 10 carbon atoms; Rf^1 is a monovalent perfluoroalkyl or perfluorooxyalkyl group; Z is a divalent hydrocarbon group of 1 to 15 carbon atoms which may contain an ether bond; subscripts a, b, c and d are integers satisfying $a \leq 3$, $b \leq 3$, $c \leq 3$, $d \leq 3$, $3 \leq a+c \leq 5$, $1 \leq b+d \leq 3$, $a+b \leq 3$, and $c+d \leq 3$, and e is independently 0 or 1.

[0013]

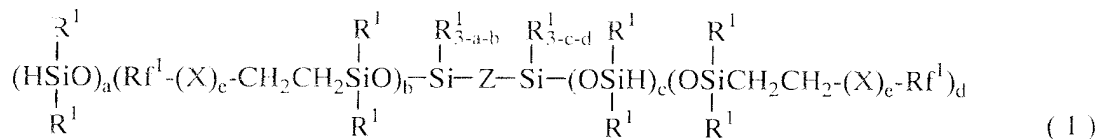


[0014]

The following is the detailed description of the invention.

The fluorinated organosilicon compound of the invention has at least one fluorinated organic group and at least three SiH groups in a molecule as shown by the general formula (1) below.

[0015]



[0016]

Herein X is independently -CH₂-, -CH₂O-, -CH₂OCH₂- or -Y-NR²-CO- wherein Y is -CH₂- or a divalent group of the following structural formula (I).

5 [0017]



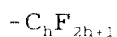
R² is hydrogen or a monovalent hydrocarbon group having 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms.

[0018]

The monovalent hydrocarbon groups represented by R² include unsubstituted monovalent hydrocarbon groups, for example, alkyl groups such as methyl, ethyl, propyl, butyl, hexyl, cyclohexyl and octyl, cycloalkyl groups, aryl groups such as phenyl and tolyl, and aralkyl groups such as benzyl and phenylethyl, and substituted monovalent hydrocarbon groups obtained by replacing some or all of the hydrogen atoms in the foregoing groups by halogen atoms such as fluorine.

[0019]

Rf¹ is a monovalent perfluoroalkyl or perfluorooxyalkyl group. The preferred monovalent perfluoroalkyl groups are of the formula:



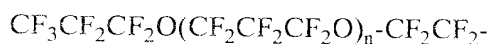
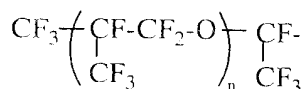
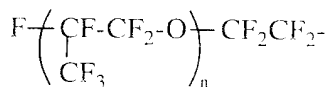
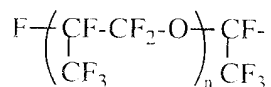
25 wherein h is an integer of 1 to 20, preferably 2 to 16.

[0020]

The monovalent perfluorooxyalkyl groups are preferably those of 1 to 500 carbon atoms, especially 1 to 300 carbon atoms. Preferred examples are given below.

30

[0021]



(n is an integer of 1 to 100.)

[0022]

Z is a divalent hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 12 carbon atoms, more preferably 1 to 10 carbon atoms, which may contain an ether bond (-O-). Examples include alkylene groups such as methylene, ethylene, propylene, methylethylene, butylene and hexamethylene, cycloalkylene groups such as cyclohexylene, and arylene groups such as phenylene, tolylene, xylylene, naphthylene and biphenylene, and combinations of any. Another example of Z is a divalent group containing an oxygen atom in the foregoing backbone structure. Herein the oxygen atom intervenes in the form of -O-.

[0023]

R¹ which may be the same or different is a monovalent hydrocarbon group having 1 to 6 carbon atoms. Illustrative are alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl and hexyl, alkenyl groups such as vinyl and allyl, and aryl groups such as phenyl. Of these, methyl and phenyl are especially preferred.

[0024]

The subscripts a, b, c and d are integers satisfying
 $a \leq 3$, $b \leq 3$, $c \leq 3$, $d \leq 3$, $3 \leq a+c \leq 5$, $1 \leq b+d \leq 3$, $a+b \leq 3$,
 and $c+d \leq 3$, so that the compound of the invention has at
 5 least one fluorinated organic group and at least three SiH
 groups in a molecule.

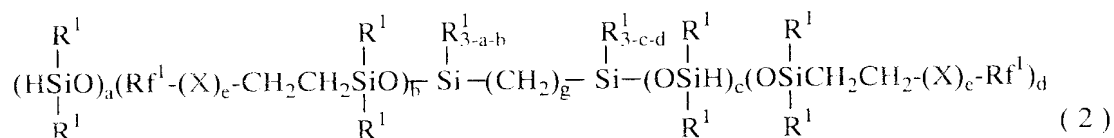
[0025]

The subscript e is independently equal to 0 or 1.

[0026]

10 Preferably, the fluorinated organosilicon compounds
 have the following general formula (2).

[0027]

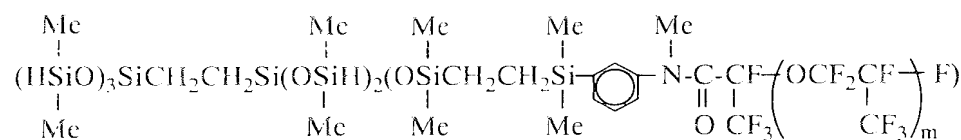
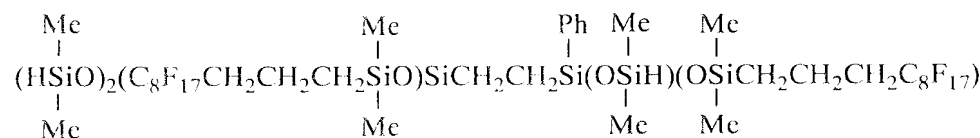
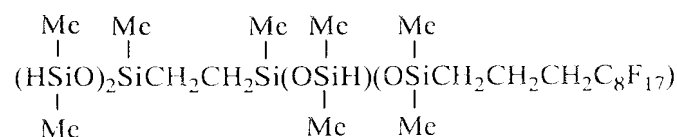
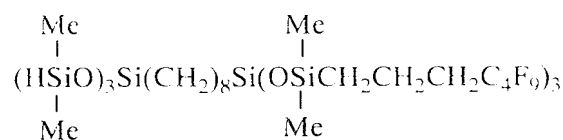
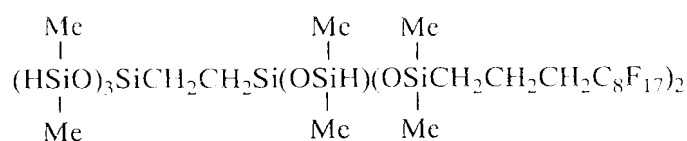


Herein R^1 , X , Rf^1 , a, b, c, d and e are as defined above and
 15 g is an integer of 1 to 8, preferably 1 to 4.

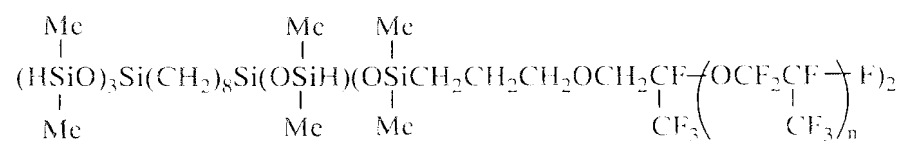
[0028]

Several exemplary fluorinated organosilicon compounds
 are given below, but the fluorinated organosilicon compounds
 of the invention are not limited thereto. Note that Me is
 20 methyl and Ph is phenyl.

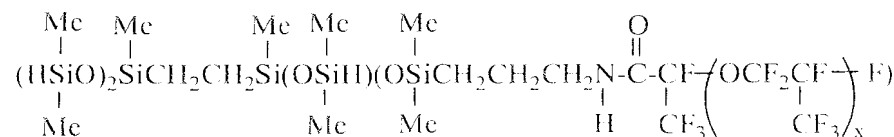
[0029]



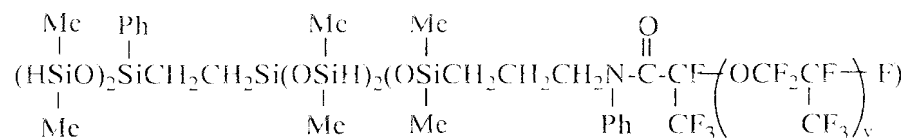
m=1~100



n=1~100



x=1~100

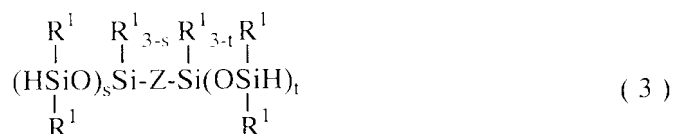


y=1~100

[0030]

The fluorinated organosilicon compound of formula (1) can be synthesized, for example, by effecting addition reaction of an alkenyl group-containing fluorine compound of the following general formula (4) to a polyfunctional SiH compound of the following general formula (3).

[0031]



Herein s and t are integers satisfying $1 \leq s \leq 3$, $1 \leq t \leq 3$, and $4 \leq s+t \leq 6$, Z and R^1 are as defined above.

10 [0032]

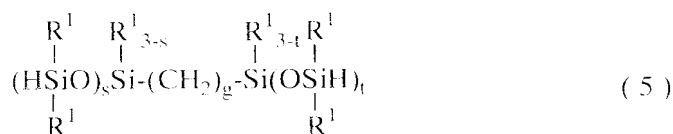


Herein Rf^1 , X and e are as defined above.

15 [0033]

Specifically, the compound of formula (2) can be obtained by effecting addition reaction of an alkenyl group-containing fluorine compound of formula (4) to a polyfunctional SiH compound of the following general formula (5) in the presence of an addition reaction catalyst such as a platinum compound.

[0034]

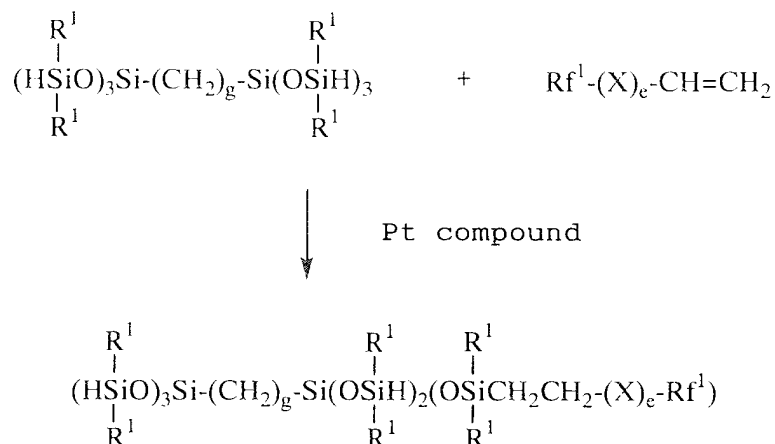


Herein, R^1 , s, t and g are as defined above.

[0035]

25 Shown below is the reaction scheme in the event where a polyfunctional SiH compound of formula (5) wherein $s = t = 3$ is used.

[0036]



Herein, R^1 , Rf^1 , X , s , t , g and e are as defined above.

[0037]

5 The synthesis of the compound of formula (1) can be carried out by the method and conditions known for addition reaction or hydrosilylation. A solvent may be used for reaction to take place. The preferred solvent is toluene, xylene, bistrifluorobenzene or the like. The amount of the
10 compound of formula (4) added to the compound of formula (3) or (5) is determined such that a , b , c and d in formula (1) or (2) fall in the above-defined range.

[0038]

15 The fluorinated organosilicon compound of the invention can be utilized not only as a crosslinking agent for addition reaction, but also as an intermediate for modification and in various other applications.

[0039]

[EXAMPLE]

20 Examples of the invention are given below by way of illustration and not by way of limitation.

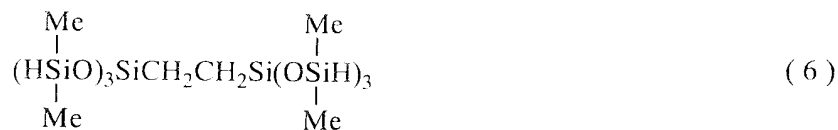
[0040]

[Example 1]

25 A 1-liter four-necked flask equipped with a stirrer, thermometer, condenser and dropping funnel was charged with 370 g of a compound of the following formula (6) and 200 g

of toluene and heated at 80°C. Thereafter, 0.1 g of a toluene solution of chloroplatinic acid-vinylsiloxane complex (platinum concentration 0.5% by weight) was added, and 700 g of a compound of the following formula (7) added dropwise from the dropping funnel.

[0041]



[0042]

After the completion of dropwise addition, the reaction solution was aged at 80°C for one hour. After the consumption of compound (7) was confirmed by gas chromatography, the reaction solution was cooled down.

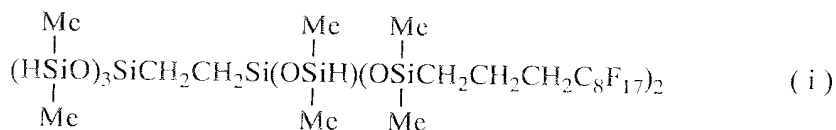
[0043]

Thereafter, 10 g of activated carbon was added to the reaction solution, which was stirred for one hour and filtered. The filtrate was stripped of the solvent under conditions of 120°C and 3 Torr, yielding 990 g of a colorless clear liquid having a viscosity of 28 cs, a specific gravity of 1.327 and a refractive index of 1.364.

[0044]

On analysis by ¹H-NMR, IR and elemental analysis, this liquid was identified to be a compound having an average structure of the following formula (i). FIG. 1 is a chart of IR analysis.

[0045]



[0046]

¹H-NMR

δ 0.09 (s, C-Si-CH₃ : 12H)

δ 0.16 (s, H-Si-CH₃ : 24H)

5 δ 0.6-1.3 (m, Si-CH₂- : 8H)

δ 1.5-2.3 (m, Si-CH₂-CH₂-CH₂- : 8H)

δ 4.72 (s, Si-H : 4H)

[0047]

IR

10 2130 cm⁻¹ ν_{Si-H}

[0048]

Elemental analysis

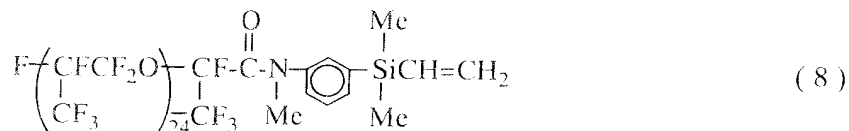
	C	H	O	Si	F
Found (%)	29.4	3.8	6.7	15.6	44.5
15 Calcd. (%)	29.7	3.9	6.6	15.4	44.4

[0049]

[Example 2]

A 1-liter four-necked flask equipped with a stirrer, thermometer, condenser and dropping funnel was charged with
 20 115 g of a compound of formula (6) and 100 g of bistrifluoromethylbenzene and heated at 80°C. Thereafter, 0.03 g of a toluene solution of chloroplatinic acid-vinylsiloxane complex (platinum concentration 0.5% by weight) was added, and 10300 g of a compound of the
 25 following formula (8) added dropwise from the dropping funnel.

[0050]



[0051]

30 After the completion of dropwise addition, the reaction solution was aged at 80°C for one hour and then cooled down.

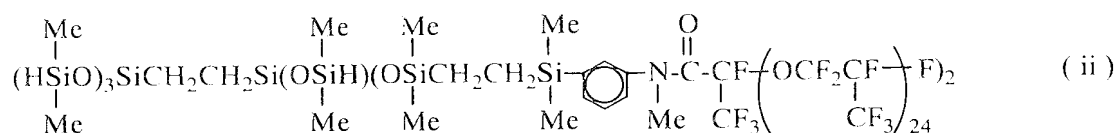
[0052]

Thereafter, 10 g of activated carbon was added to the reaction solution, which was stirred for one hour and filtered. The filtrate was stripped of the solvent under conditions of 120°C and 3 Torr, yielding 1050 g of a colorless clear liquid having a viscosity of 2520 cs, a specific gravity of 1.709 and a refractive index of 1.333.

[0053]

On analysis by ¹H-NMR, IR and elemental analysis, this liquid was identified to be a compound having an average structure of the following formula (ii). FIG. 2 is a chart of IR analysis.

[0054]



[0055]

¹H-NMR

δ 0.09 (s, C-Si-CH₃: 6H)
 δ 0.16 (s, H-Si-CH₃: 3CH)
 δ 0.31 (s, arom. Si-CH₃: 6H)
 δ 0.6-1.3 (m, Si-CH₂-: 8H)
 δ 3.23 (s, N-CH₃: 3H)
 δ 4.72 (s, Si-H: 5H)
 δ 7.2-7.7 (m, arom.: 4H)

[0056]

IR

2130 cm⁻¹ ν_{Si-H}

[0057]

Elemental analysis

	C	H	O	Si	F	N
Found (%)	24.9	1.4	10.3	5.1	58.0	0.3
Calcd. (%)	24.7	1.3	10.2	5.2	58.3	0.3

[0058]

[Effect of the Invention]

The fluorinated organosilicon compounds of the present invention is capable of hydrosilylation reaction with such
5 compounds as vinyl group-bearing fluoro-polymers in a stable manner and fully compatible therewith.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1]

A diagram showing an IR absorption spectrum of the
10 compound synthesized in Example 1.

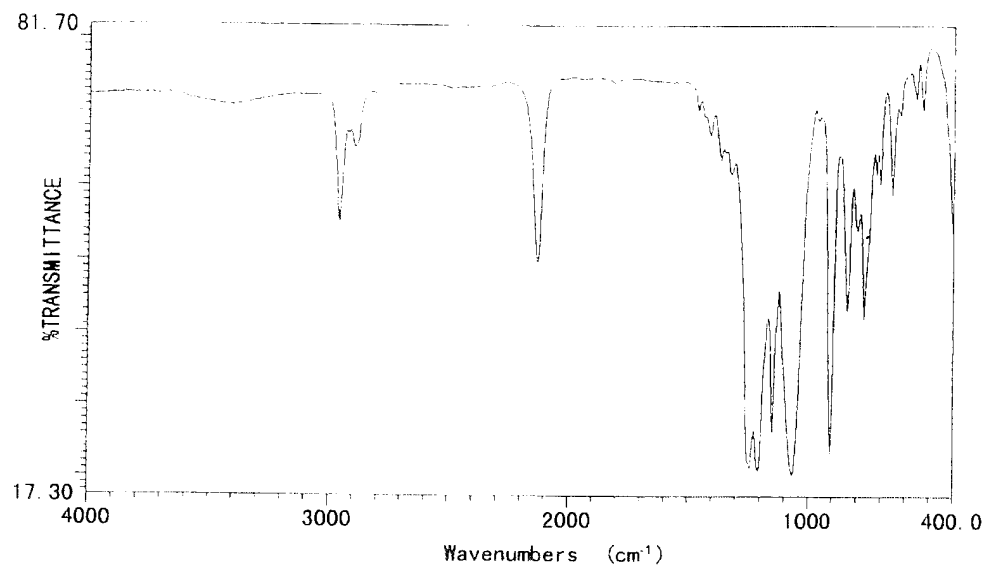
[FIG. 2]

A diagram showing an IR absorption spectrum of the compound synthesized in Example 2.

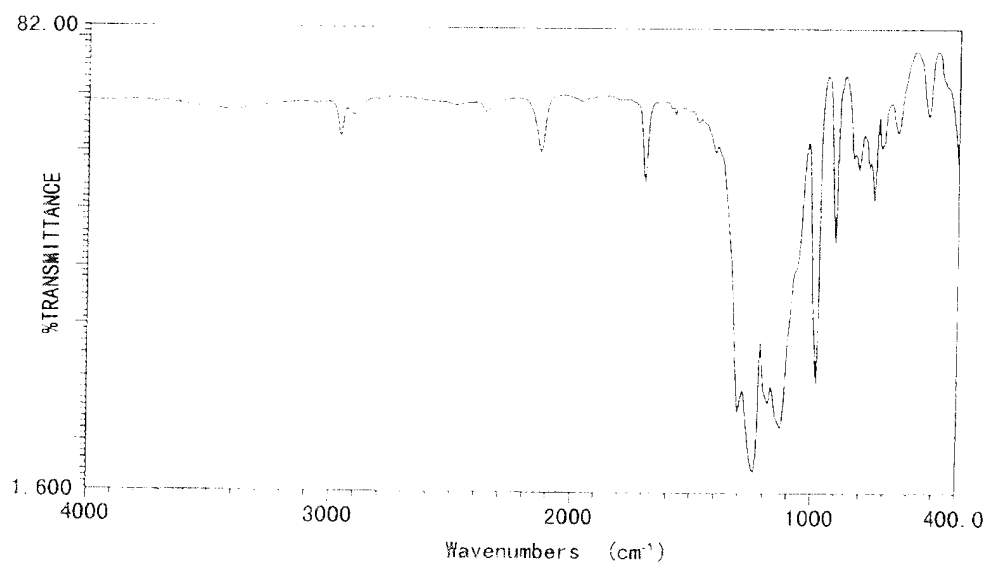
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[DRAWING]

[FIG. 1]



[FIG. 2]

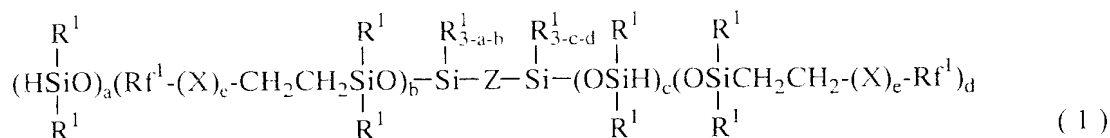


2001-042717

[ABSTRACT]

[Means for Solution]

A fluorinated organosilicon compound having the following
5 general formula (1):



wherein R¹ is independently a monovalent hydrocarbon group having
1 to 6 carbon atoms,

X is independently -CH₂-, -CH₂O-, -CH₂OCH₂- or -Y-NR²-CO-
10 wherein Y is -CH₂- or a divalent group of the following structural
formula (I), and R² is hydrogen or a monovalent hydrocarbon group
having 1 to 10 carbon atoms,

Rf¹ is a monovalent perfluoroalkyl or perfluorooxyalkyl
group,

15 Z is a divalent hydrocarbon group of 1 to 15 carbon atoms
which may contain an ether bond,

subscripts a, b, c and d are integers satisfying
a ≤ 3, b ≤ 3, c ≤ 3, d ≤ 3, 3 ≤ a+c ≤ 5, 1 ≤ b+d ≤ 3, a+b ≤ 3,
and c+d ≤ 3, and e is independently 0 or 1:



20 [Effect]

The fluorinated organosilicon compounds of the present
invention is capable of hydrosilylation reaction with such
compounds as vinyl group-bearing fluoro-polymers in a stable manner
and fully compatible therewith.

25 [Selected Drawing] none